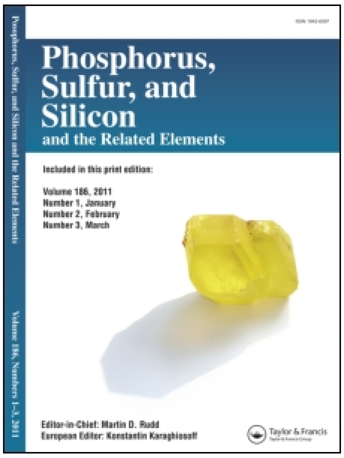

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A NEW CLASS OF BIOLOGICALLY ACTIVE DIORGANOSILICON(IV) COMPLEXES

Anita Phor[a]; I. Singh[a]; J. S. Phor[b]
[a] Department of Chemistry, M.D. University, Rohtak, India [b] Department of Physics, C.R.A. College, Sonepat, India

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A NEW CLASS OF BIOLOGICALLY ACTIVE DIORGANOSILICON(IV) COMPLEXES

ANITA PHOR and I. SINGH
Department of Chemistry, M.D. University, Rohtak-124001, India

and

J. S. PHOR
Department of Physics, C.R.A. College, Sonepat-131001, India

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The present paper describes the synthesis, structural features and antimicrobial activity of some newly synthesized diorganosilicon(IV) complexes with benzothiazolines derived from ketones. The resulting complexes have been subjected to elemental analyses, conductance measurements, molecular weight determination and electronic, infra-red, ^{13}C and ^{1}H NMR spectral studies and their plausible structures have been discussed. Spectral data support a five-coordinate presumably trigonal bipyramidal geometry for 1:1 complexes, whereas 1:2 complexes are six-coordinated with an octahedral geometry. A few representative complexes along with their ligands have also been screened for their fungicidal as well as insecticidal activities and found to be quite active in this respect.

Key words: Diorganosilicon (IV)-benzothiazolines complexes, synthesis, structural and antimicrobial activity studies.

INTRODUCTION

In recent years, there has been tremendous activity in the chemistry of main group elements as well. The main interest has been in the chemistry of silicon, tin and lead and which has been found to have far reaching implications throughout the domain of chemistry. A number of research articles dealing with a variety of applications of these compounds are now available in the literature.[1-5] Commercially, the organoderivatives of these elements have gained wide uses in the field of agriculture, medicine and industry.[6-8] Organosilicon compounds with nitrogen and sulfur donor ligands have been the subject of patents due to their biological importance. A variety of complex compounds containing silicon-sulfur linkage and having biological importance are known.[9-11] During the course of present investigations, reactions of diphenylsilanediol with heterocyclic benzothiazolines have been carried out and the results of these studies have been discussed in the present paper.

RESULTS AND DISCUSSION

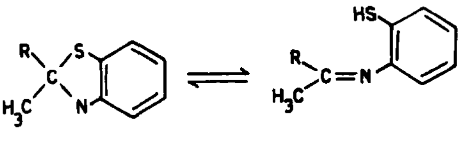
The reactions of diphenylsilanediol with the benzothiazolines derived from heterocyclic ketones and 2-aminothiophenol have been carried out in 1:1 and 1:2

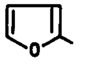
molar ratios in dry benzene. These reactions can be represented by the following general equations:

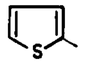
$$Ph_2Si(OH)_2 + \widehat{NS}H \xrightarrow{C_6H_6} Ph_2SiOH(\widehat{NS}) + H_2O$$

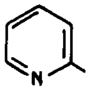
$$Ph_2Si(OH)_2 + 2\widehat{NS}H \xrightarrow{C_6H_6} Ph_2Si(\widehat{NS}) + 2H_2O$$

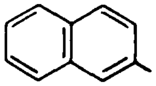
where $\widehat{NS}$ represents the donor set of the ligands. The following ligands were used:



R =  = 2-Ac Fur. Bzt H

 = 2- Ac Thiop. Bzt H

 = 2-Ac Pyd. Bzt H

 =2-Ac Naph. Bzt H

All the resulting products are colored solids having sharp melting points. These are soluble in DMSO, DMF, T.H.F. and methanol. The molecular weights determined by the Rast-camphor method correspond with the formula weights indicating their monomeric nature. The low values of molar conductance of 10^{-3} M solutions (10–15 ohm^{-1} cm^2 mol^{-1}) in dry DMF show them to be non-electrolytes. The mode of bonding of benzothiazolines to the silicon atom has been established on the basis of the following spectroscopic studies.

Electronic Spectra

The UV spectra of the benzothiazolines consists of two broad, strong bands around 280 nm and 310 nm, characteristic of the cyclic (benzothiazoline) form of the ligands. These may be attributed to the $Ø - Ø^*$ and $\pi - \pi^*$ (benzenoid) transitions, respectively.

A new band around 400 nm due to $n - \pi^*$ electronic transitions of the azomethine group is observed in the spectra of silicon complexes. This suggests the formation of azomethine grouping on complexation and thus isomerization of the ligands into the Schiff-base form in presence of a silicon atom.

IR Spectra

In the IR spectra of benzothiazolines, the absence of absorption bands at ca. 2650 and 1620 cm^{-1} due to ν (SH) and $\nu\left(\mathrm{>C{=}N}\right)$ vibrations, respectively indicates the existence of the ligands in the benzothiazoline[12] form rather than Schiff-base form. In the spectra of the complexes, the bands in the region, 3300–3100 cm^{-1} due to the NH stretching vibrations[13] of the ligands remain absent and a new band at ca. 1615 cm^{-1} is observed due to $\nu\left(\mathrm{>C{=}N}\right)$ vibrations. The appearance of this band suggests that the resulting complexes are the Schiff-base derivatives of silicon. The chelation of ligands through azomethine nitrogen and thiolo sulfur gets further support by the appearance of new bands in the regions, 575–550 and 530–520 cm^{-1} due to ν (Si—N)[14] and ν (Si—S)[15] vibrations, respectively. Medium to strong intensity bands at ca. 1425, 1120, 725 and 700 cm^{-1} are due to ν (Si—C_6H_5),[16] vibrations. The band of medium intensity at ca. 3500 cm^{-1} may be assigned to ν (OH) vibrations.

^{1}H NMR Spectra

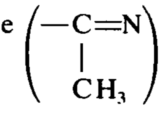
The proton magnetic resonance spectra of ligands along with their corresponding diorganosilicon(IV) complexes have been recorded in $CDCl_3$. The chemical shift values of different protons have been recorded in Table I.

For the sake of convenience the spectra of 2-AcPyd.BztH and its corresponding diphenylsilicon complexes have been discussed in details. The NH proton signal of monofunctional bidentate benzothiazoline appears at δ, 4.55 ppm. This, how-

TABLE I

^{1}H NMR spectral data (δ, ppm) of ligands and their corresponding diphenylsilicon(IV) complexes

Compound	-NH	$-\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C{=}N}}}$	Aromatic	Si-Ph
2-AcPyd.BztH	4.55	2.15	7.55 - 6.70	-
2-AcFur.BztH	4.38	1.95	7.50 - 6.75	-
2-AcThiop.BztH	4.42	2.10	7.60 - 6.52	-
2-AcNaph.BztH	4.50	2.06	7.52 - 6.60	-
Ph$_2$SiOH(2-AcPyd.Bzt)	-	2.38	7.65 - 6.78	5.90
Ph$_2$Si(2-AcPyd.Bzt)$_2$	-	2.42	7.70 - 6.82	6.15
Ph$_2$SiOH(2-AcFur.Bzt)	-	2.25	7.72 - 6.75	6.05
Ph$_2$Si(2-AcFur.Bzt)$_2$	-	2.28	7.76 - 6.80	6.10
Ph$_2$SiOH(2-AcThiop.Bzt)	-	2.36	7.75 - 6.70	6.18
Ph$_2$Si(2-AcThiop.Bzt)$_2$	-	2.41	7.84 - 6.78	6.22
Ph$_2$SiOH(2-AcNaph.Bzt)	-	2.30	7.77 - 6.83	6.00
Ph$_2$Si(2-AcNaph.Bzt)$_2$	-	2.35	7.83 - 6.86	6.12

ever, disappears in the case of silicon complexes indicating the complete removal of proton from NH group and coordination of nitrogen with simultaneously covalent bond formation by sulfur with silicon. The protons due to the  $\left(\begin{array}{c}-\mathrm{C}{=}\mathrm{N}\\ |\\ \mathrm{CH_3}\end{array}\right)$ group appear at δ, 2.15 ppm and show a downfield shift (δ, 2.38 and 2.42 ppm in 1:1 and 1:2 complexes, respectively) on complex formation. The aromatic protons are observed in the region, δ, 7.81–6.77 ppm in the complexes.

^{13}C *NMR Spectra*

The ^{13}C NMR spectra of 2-AcPyd.BztH and its complexes have also been recorded in dry DMSO (Table II). The noticeable shift observed in the positions of carbons attached to the azomethine nitrogen and thiolic sulfur supports the involvement of these groups in the bond formation.

On the basis of the above spectral evidence, the following trigonal bipyramidal and octahedral geometries have been proposed for the 1:1 (Figure 1) and 1:2 derivatives (Figure 2) respectively.

TABLE II

^{13}C NMR spectral data (δ, ppm) of ligands and their corresponding diphenylsilicon(IV) complexes

Compound	Chemical Shift Values				
	1	2	3	Aromatic carbons	$Si-C_6H_5$
2-AcFur.BztH	146.6	13.8	142.5	120.4,121.8,122.3,123.7 126.5,127.2,127.8,128.5	-
Ph_2SiOH(2-AcFur.Bzt)	159.0	15.2	154.6	121.7,122.6,123.5,124.2 127.0,127.8,128.4,129.6	131.5,134.2 136.7,137.5
Ph_2Si(2-AcFur.Bzt)$_2$	161.6	15.7	155.8	122.3,123.5,123.8,124.5 127.6,128.8,129.0,129.3	132.7,135.3 137.2,138.0
2-AcPyd.BztH	151.2	13.1	139.6	123.2,121.3,120.4,121.8 125.2,126.5,125.6,125.8	-
Ph_2SiOH(2-AcPyd.Bzt)	162.8	14.5	156.2	124.5,122.0,121.4,122.5 125.8,127.3,126.5,126.9	133.6,134.0 136.8,138.0
Ph_2Si(2-AcPyd.Bzt)$_2$	164.7	15.0	157.6	125.8,123.7,122.0,123.0 125.8,127.3,126.5,126.9	135.0,137.5 139.0,140.5

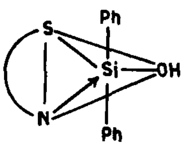


FIGURE 1

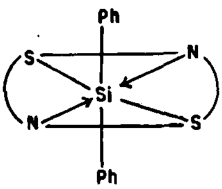


FIGURE 2

Biocidal Activity

The antifungal activity of two ligands, 2-AcPyd.BztH and 2-AcThiop.BztH along with their silicon complexes, was evaluated against Helminthosporum graminium and Alternaria alternata at two different concentrations. The results have been summarized in Table III. The above two ligands and their silicon complexes were also screened for their insecticidal activity against adult male and female cockroaches (Table IV). It is clear from the fungicidal and insecticidal screening data that all the silicon complexes are more toxic than the parent ligands. The greater antimicrobial activity of the complexes than the ligand can be explained by the greater lipophilic character of the complexes so they can pass through the lipoid layers of the organism cell membrane and thus interfere in the normal cell processes.[17,18] However, the results show that the biocidal activity of ligands and their complexes decreases on lowering the concentrations.

TABLE III
Fungicidal activity of ligands and their diphenylsilicon(IV) complexes

Compound	Average percentage inhibition after 7 days			
	Helminthosporium graminium		Alternaria alternata	
	0.01% (conc.)	0.1% (conc.)	0.01% (conc.)	0.1% (conc.)
2-AcPyd.BztH	40.5	59.7	38.2	60.5
2-AcThiop.BztH	43.8	61.6	41.0	65.7
Ph$_2$SiOH(2-AcPyd.Bzt)	65.5	79.3	60.8	80.5
Ph$_2$Si(2-AcPyd.Bzt)$_2$	69.7	84.4	62.4	87.3
Ph$_2$SiOH(2-AcThiop.Bzt)	70.2	88.5	68.2	90.6
Ph$_2$Si(2-AcThiop.Bzt)$_2$	73.8	92.6	70.7	95.4

TABLE IV
Insecticidal activity of ligands and their diphenylsilicon(IV) complexes

Compound	Average percentage inhibition after 7 days	
	0.01% (conc.)	0.1% (conc.)
2-AcPyd.BztH	26.5	40.2
2-AcThiop.BztH	29.0	42.8
Ph$_2$SiOH(2-AcPyd.Bzt)	50.6	65.8
Ph$_2$Si(2-AcPyd.Bzt)$_2$	55.7	70.4
Ph$_2$SiOH(2-AcThiop.Bzt)	58.3	72.5
Ph$_2$Si(2-AcThiop.Bzt)	61.7	75.20

EXPERIMENTAL

All manipulations were carried out under anhydrous conditions and the chemicals used were dried and distilled before use.

Preparation of Ligands

The ligands were prepared by the condensation of heterocyclic ketones (i) 2-acetylfuran, (ii) 2-acetylpyridine, (iii) 2-acetylthiophene, (iv) 2-acetylnaphthalene with 2-aminothiophenol in equimolar ratio in alcohol. These were characterized by elemental analyses, melting point, IR and NMR spectra studies. The physical characteristics of these ligands are given below:

Ligand	Colour	State	m.p. (°C)
a) $C_{12}H_{11}NSO$	Yellow	Solid	84
b) $C_{12}H_{11}NS_2$	Yellow	Solid	85
c) $C_{13}N_{12}N_2S$	Yellow	Solid	87
d) $C_{18}N_{15}NS$	Yellow	Solid	88

Synthesis of Diphenylsilicon(IV) *Complexes*

To a weighted amount of diphenylsilanediol (0.6–1.25 gm) in benzene was added the requisite amount of the ligand in 1:1 and 1:2 molar ratios and the contents were refluxed for about 15–18 hours and the liberated water was removed azeotropically with benzene. The resulting product, was then isolated by removing the excess of the solvent under reduced pressure and dried for 3–4 hours in vacuo. The complexes were repeatedly washed with dry cyclohexane so as to ensure their purity and again dried under reduced pressure. Their purity was further checked by T.L.C. using silica gel-G. The analytical data and physical properties of the resulting products have been reported in Table V.

Analytical Methods and Physical Measurements

Carbon and hydrogen analyses were performed at the microanalytical laboratory of the department. Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods, respectively. Conductivity was measured at 32 ± 1°C with a conductivity bridge type, 304 systronics model and the molecular weights were determined by the Rast-camphor method. IR spectra were recorded on a Perkin-Elmer

TABLE V

Physical characteristics and elemental analyses of diphenylsilicon(IV) complexes

Reactants		Product formed and colour	M.P. (°C)	Elemental analysis (%)					Mol.Wt. Found (Calcd.)
Starting material (gm)	Ligand (gm)			C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	Si Found (Calcd.)	
$Ph_2Si(OH)_2$	$C_{12}H_{11}NSO$	$C_{24}H_{21}NSO_2Si$	154	69.01	5.22	3.43	7.48	6.68	439.46
1.02	1.02	Dirty yellow		(69.36)	(5.09)	(3.36)	(7.72)	(6.76)	(415.59)
$Ph_2Si(OH)_2$	$C_{12}H_{11}NSO$	$C_{36}H_{30}N_2S_2O_2Si$	172	70.11	4.68	4.33	10.14	4.35	635.50
0.72	1.45	Dark brown		(70.32)	(4.92)	(4.55)	(10.43)	(4.57)	(614.86)
$Ph_2Si(OH)_2$	$C_{12}H_{11}NS_2$	$C_{24}H_{21}NS_2OSi$	180	66.46	4.78	3.36	14.49	6.32	405.43
1.10	1.18	Light brown		(66.78)	(4.90)	(3.24)	(14.86)	(6.50)	(431.66)
$Ph_2Si(OH)_2$	$C_{12}H_{11}NS_2$	$C_{36}H_{30}N_2S_4Si$	109	66.38	4.84	4.12	19.44	4.13	670.35
0.76	1.64	Dark brown		(66.83)	(4.69)	(4.33)	(19.82)	(4.34)	(646.99)
$Ph_2Si(OH)_2$	$C_{13}H_{12}N_2S$	$C_{25}H_{22}N_2SOSi$	130	70.64	5.55	6.38	7.49	6.43	448.38
1.13	1.19	Dark yellow		(70.39)	(5.19)	(6.57)	(7.52)	(6.58)	(426.61)
$Ph_2Si(OH)_2$	$C_{13}H_{12}N_2S$	$C_{38}H_{32}N_4S_2S_i$	185	71.24	5.30	8.47	10.32	4.26	658.61
1.26	2.66	Light yellow		(71.66)	(5.06)	(8.79)	(10.07)	(4.41)	(636.92)
$Ph_2Si(OH)_2$	$C_{18}H_{15}NS$	$C_{30}H_{25}NSOSi$	176	75.46	5.48	2.68	6.62	5.84	445.88
0.88	1.13	Yellowish brown		(75.75)	(5.30)	(2.99)	(6.74)	(5.91)	(475.69)
$Ph_2Si(OH)_2$	$C_{18}H_{15}NS$	$C_{48}H_{38}N_2S_2Si$	137	78.81	5.40	3.95	8.66	3.78	710.18
0.64	1.65	Reddish brown		(78.43)	(5.21)	(3.81)	(8.72)	(3.82)	(735.07)

577 grating spectrophotometer with KBr optics. The electronic spectra of the compounds were obtained on a Pye-Unicam SP-8-100 spectrophotometer in dry methanol. The ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer in $CDCl_3$ using TMS as the internal standard at 89.55 and 22.49 MHz, respectively.

Biological Screening

The antifungal activity of the ligands and their diphenylsilicon(IV) complexes was evaluated by the Agar plate technique.[19] The percentage inhibition given in Table III was calculated using the following formula,

$$\% \text{ inhibition} = \frac{(C - T) \times 100}{C}$$

where C = diameter of the fungus colony in control after 5 days and T = diameter of the fungus colony in tested plate after the same period. The insecticidal activity against adult male and female cockroaches was tested by the typical method of application using a micrometer syringe.[20]

ACKNOWLEDGEMENTS

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